

## STORAGE STABILITY OF DISTILLATE DIESEL FUELS: CHANGES IN PHENALENE AND PHENALENONE CONCENTRATIONS DURING LONG TERM AMBIENT STORAGE

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### INTRODUCTION

Unstable distillate fuels can degrade during storage forming insoluble sediment and darkening in colour. Pedley, Hiley and Hancock<sup>1,2</sup> have proposed a reaction mechanism to account for the production of the majority of the sediment, in which indoles react with phenalenones to form soluble sediment precursors (indolylphenalenes and indolylphenalenones) which in turn react with acids to form sediment. The chemistry is complex; a simplified mechanism is shown in Figure 1.

Methods of analysis have been developed to quantify phenalenes and phenalenones directly in fuels to low ppm levels<sup>3,4</sup>. Application of these methods to a number of fuels has shown that phenalenes and phenalenones are not present in stable straight run fuels, but are present in a number of cracked fuels. The total concentration of phenalenes and phenalenones may be as high as 0.1%, although blends containing cracked stocks generally exhibit much lower concentrations.

Previous trials<sup>5</sup> have shown that the phenalenes content of an unstable catalytically cracked stock diminished from approximately 0.1% to zero over a period of a year, while the phenalenones content increased. From these trials it became apparent that neither the phenalenes/phenalenones nor indoles contents were necessarily the limiting factors in sediment production. However the trials gave no information on the rate of depletion of the phenalenes, the rate of increase of the phenalenones or the relationship of the concentrations of these species to the production of sediment.

This paper describes the changes in phenalene and phenalenone concentrations of an unstable fuel blend with time, and examines any correlation between these concentrations, sediment levels and colour.

### EXPERIMENTAL

A research blend consisting of 50% fresh catalytically cracked gas oil and 50% fresh straight run gas oil (both from North Sea crude stocks) was subjected to long term storage at ambient temperatures in 50 litre vented non-lacquer lined mild steel drums, and sub-sampled for compositional data.

The stability of the blend was assessed initially using ASTM D2274, ASTM D525/D381 modified (16 hours at 100°C in oxygen), an in-house method (3 days at 80°C) and also using ASTM D4625 (storage for 16 weeks at 43°C). The sediment in the latter tests was measured at 4 weekly intervals.

The phenalenes and phenalenones concentrations of the blend were monitored using chromatographic methods<sup>3,4</sup>. The phenalenes were determined using reverse phase HPLC with electrochemical detection to selectively quantify the phenalene species. Phenalenones were measured using normal phase HPLC selectively detecting these compounds by UV absorbance at 400nm. Filterable sediment levels and colour (ASTM D1500) were also monitored at intervals.

## RESULTS AND DISCUSSION

### Accelerated storage tests.

Results from the ASTM D2274 tests imply that the fuel blend was stable, with  $<0.1$  mg/100ml total insolubles formed during the ageing period (Table 1). Similar results were obtained from the in-house method (3 days at  $80^{\circ}\text{C}$ ). Very high levels of gum were predicted by ASTM D525/D381. These tests were therefore considered unsuitable for predicting storage stability. The results of the ASTM D4625 test indicate that the fuel produced  $<2$  mg/100ml insolubles during the first four week period but thereafter there was a rapid increase to about 12 mg/100ml after 16 weeks (Fig 2, Table 1).

### Ambient storage

#### Filtered sediment

There appears to have been an induction period of between 16 and 20 weeks during which sediment formation was less than 2mg/100ml. Thereafter there was a rapid increase in sediment in the fuel, rising to about 17mg/100ml after 50 weeks storage (Fig 3, Table 2).

An attempt was made to relate the sediment formed in the ambient drum storage to levels predicted in the ASTM D4625 tests. It has been assumed that 1 week at  $43^{\circ}\text{C}$  is equivalent to 4 weeks storage under ambient conditions. The data show (Table 2) that within the precision of the test procedures, there is some correlation, particularly up to 40 weeks storage. Thereafter, sediment increased at a faster rate in the drum storage and after 50 weeks storage, the level of sediment was greater by a factor of 2 over predicted levels. Although absolute levels of sediment were not predicted accurately, the figures indicated the overall likely stability of the blend.

#### Phenalenenes concentration changes

The initial concentration of phenalenenes (phenalene and its alkyl homologues) in the untreated blend was high at  $850\text{ mg l}^{-1}$ . The phenalenenes concentrations diminished with time and were still present at about  $100\text{ mg l}^{-1}$  after one year's storage (Table 3, Figure 4). The results indicate that the oxidation of the phenalenenes approximates to a pseudo-first order reaction in the fuel (Figure 5). This conclusion should be treated with caution, however, as the exact mechanism of phenalene oxidation has not yet been established. The phenalenyl radical has been observed in diesel fuels<sup>1,12</sup> and is probably involved in the reaction mechanism in hydrocarbon fuels. It has not yet been established whether phenalenones are produced directly from the radical, or whether further intermediates, such as the hydroxyphenalenenes, could also be involved. Phenalenenes are also produced as a byproduct of the condensation reaction producing indolylphenalenenes and indolylphenalenones<sup>8</sup>, thus continually modifying the phenalenenes concentration with time. The related compound benzantracene was initially present at  $100\text{ mg l}^{-1}$  (the homologues of this compound were not quantified), and although not quantified throughout the storage period, appeared to diminish in a similar way to the phenalenenes.

The phenalene homologues exhibited a similar distribution to that seen in other fuels containing 'fresh' catalytically cracked stock, namely that the major constituents were the monomethylphenalenenes (about 50% of the initial total phenalene content), followed by the dimethyl or ethyl substituted phenalenenes, at about 40%. Phenalene itself comprised only a small proportion of the total phenalene content - approximately 12% (Table 3).

### Phenalenones concentration changes

The phenalenones concentrations were initially low at  $15\text{mg l}^{-1}$  total phenalenones, with phenalene itself the major constituent (Table 4). The general pattern of phenalenones distribution previously observed in other fuels was noted in this blend and was consistent throughout the storage period: phenalene as the major constituent, approximately 40% of the total phenalenones concentration, followed by the 2-, 5-, and 8-methyl derivatives at about 30% to 50% of the phenalene concentration, and the remaining methyl homologues at low concentrations. The concentration of 9-methylphenalene remained at trace levels only,  $2\text{mg l}^{-1}$  being the highest concentration recorded. The dimethyl or ethylphenalenones and higher homologues were not quantified. However, there are no large peaks in the phenalene chromatogram unaccounted for. It may therefore be reasonably assumed that unless the dimethyl homologues have considerably lower absorbances at  $400\text{nm}$  than phenalene, these compounds are not a major proportion of the total phenalenones found in fuels. The related benzantrones were present at all times at considerably lower concentrations than the phenalenones (Table 4), with benzantrone the major constituent.

There appeared to be an induction period of two to three weeks where the ketones concentrations remained static, after which the concentrations gradually increased. After about 13 weeks the total phenalenones concentrations increased markedly before beginning to plateau out (Figure 6). The benzantrones acted in a similar fashion. It is interesting to note that the concentration of 2-methylphenalene was initially very similar to that of the 5- and 8-methyl homologues, but with time the 2-methylphenalene content increased at a faster rate than its isomers (Figure 7). After a year the concentration of the 2-methylphenalene was approximately double that of the 5- and 8-substituted isomers. This reflects model compound studies<sup>9</sup> where 2-methylphenalene was found not to react with indoles in acid conditions.

The concentrations of phenalene and the methylphenalenones always appeared less than the initial concentrations of phenalene and monomethylphenalenes respectively. As with previous model studies<sup>9</sup>, the mass balance for the phenalene species is difficult to reconcile, only approximately 50% of the initial phenalenes being accounted for from the measurement of phenalene, phenalenones and sediment (estimating the contribution from phenalene species in the sediment to be about 35% of the mass). Known products include phenalenones, indolylphenalenes and indolylphenalenones, and salts of these products which comprise a large proportion of the sediment. Phenalenones<sup>11</sup> may also be produced during the reaction with indoles which would in part account for the discrepancy.

### Colour and sediment changes

The data indicate a gradual deterioration in colour during the first 20 weeks of storage followed by a period of little change (Table 2, Figure 8). There appears to be a correlation between colour and phenalenones concentrations. The relationship appears to be linear from the available data (Figure 9). The increase in concentration of the coloured ketones with time would contribute to the darkening of fuel during storage and to the formation of the fuel-soluble sediment precursors. The darkening in colour is believed to be more attributable to the formation of the latter and it would be informative to quantify the precursors for this reason.

The relationship between sediment levels and phenalenones concentration is demonstrated in Figure 10. The relationship appears to be linear for this fuel blend, with a sharp change in gradient when the total phenalenones concentration reaches approximately  $130\text{mg l}^{-1}$  - equivalent to about thirteen weeks storage. A similar correlation is obtained between sediment levels and the concentration of phenalenones excluding those substituted in the 2-position. The relationship follows the same pattern as for total phenalenones, and there is a sharp change in gradient at about  $100\text{mg l}^{-1}$  phenalenones - again, equivalent to about thirteen weeks storage.

Studies of previous trials<sup>4,6</sup> have shown that the strong acid content of fuels starts to increase after similar periods of storage and it is possible that increased production of strong acids such as aromatic sulphonic acids will enhance the rate of sediment production. The initial thiol content of the fuel was low (0.0007% m mercaptan sulphur) and the fuel blend contained negligible strong acid (<0.05mg KOH.l<sup>-1</sup> by conductometric titration<sup>6</sup>) throughout the storage trial. The concentrations of indoles and phenalenes/phenalenones were very high and it might be expected that the strong acids appeared to be entirely consumed in the production of sediment (Figure 1), indicating that the acidity of the fuel was the limiting factor in the sediment forming process for this fuel.

## CONCLUSIONS

There was no correlation between results from accelerated ageing tests at high elevated temperature and levels of sediment produced during natural ageing. Reasonable correlation was obtained with results by ASTM D4625, ageing for 16 weeks at 43°C.

Phenalenes appeared to deplete by a pseudo- first order reaction at ambient temperatures. The reaction possibly proceeds via radical formation but further details of the mechanism are not known ie whether intermediates such as the hydroxyphenalene are produced. The order of reaction obtained should be treated with caution as phenalenes may also be produced as byproducts from the phenalene/indole condensation reaction. The concentrations of the phenalenes and the benzanthrone increased with time to a plateau. The concentration of 2-methylphenalene reached higher concentrations than the 5- and 8-methylphenalenes, consistent with model studies showing that this compound does not react with indoles.

Colour and sediment levels appear to follow the same trend as phenalene concentration. There appear to be direct correlations between the colour and sediment produced and the concentration of phenalenes for this fuel blend. More fuels from different sources should be examined to confirm this. The limiting factor in sediment formation for this fuel appeared to be the acidity of the fuel, in particular the availability of strong acids.

## REFERENCES

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TABLE 1 - RESULTS OF ACCELERATED AGEING TESTS

Analysis	Week	Result	Analysis	Week	Result
Filtered Sediment			ASTM D4625		
GFC Paper	0	0.1	Filterable Insolubles mg/100ml	0	<0.1
Colour ASTM D1500	0	<3	Adherent Insolubles mg/100ml	0	<0.1
			Total Insolubles mg/100ml	0	<0.1
ASTM D2274			Filterable Insolubles mg/100ml	4	0.7
Filtered Insolubles mg/100ml	0	<0.1	Adherent Insolubles mg/100ml	4	0.3
Adherent Insolubles mg/100ml	0	<0.1	Total Insolubles mg/100ml	4	1.0
Total Insolubles mg/100ml	0	<0.1	Filterable Insolubles mg/100ml	8	2.8
ASTM D525 (modified)			Adherent Insolubles mg/100ml	8	2.1
Potential gum	0	226	Total Insolubles mg/100ml	8	4.9
After heptane wash	0	225	Filterable Insolubles mg/100ml	12	1.8
Colour after ageing	0	4.5	Adherent Insolubles mg/100ml	12	6.1
			Total Insolubles mg/100ml	12	7.9
80°C STORAGE (MOD method)			Filterable Insolubles mg/100ml	16	4.0
Insolubles mg/l	0	2	Adherent Insolubles mg/100ml	16	6.9
			Total Insolubles mg/100ml	16	10.9

TABLE 2 - FILTERED SEDIMENT AND COLOUR MEASURED DURING AMBIENT STORAGE

Week no	Filtered Sediment Measured	mg/100ml Predicted	Colour ASTM D1500
0	1.1		<3.0
4	0.2		2.5
8	0.7		<4.0
12	1.1		4.0
16	1.1	1.0	5.5
20	2.5		5.5
24	4.7	3.0	5.5
28	7.5		5.5
32	6.6	4.9	6.0
36	10.9		6.0
40	9.2	6.4	6.0
50	16.8	8.3	7.0

TABLE 3 - CHANGES IN PHENALENES CONCENTRATIONS WITH TIME

Time wks	Phenylene mg l <sup>-1</sup>	C1 Phenalenes mg l <sup>-1</sup>	C2 Phenalenes mg l <sup>-1</sup>	Total Phenalenes mg l <sup>-1</sup>
1.5	115	445	300	860
2	105	395	250	750
8	65	245	140	450
13	70	220	100	390
18	75	350	170	595
24	55	230	135	420
30	35	150	75	260
36	30	115	55	200
40	20	60	30	110
46	20	75	40	135

TABLE 4 - CHANGES IN PHENALENONES CONCENTRATIONS WITH TIME

Time wks	Phenalenones concentrations in mg l <sup>-1</sup>								Total Phenalenones mg l <sup>-1</sup>	Total Benzanthrones mg l <sup>-1</sup>
	Phenalenone	2-Me	Phenalenone Homologues 3 & 4-Me 5-Me 6-Me				7-Me	8-Me	9-Me	
1.5	6	2.8	0.9	2.7	ND	ND	2.6	ND	15	0.2
2	6	3.4	0.9	3.2	0.1	0.4	3.0	ND	17	0.2
4	6	5.4	0.4	3.0	0.1	0.1	3.0	ND	19	0.2
6	15	8.5	4.0	6.0	1.6	1.0	4.0	0.3	40.5	4.0
8	15	14	3.0	7.0	1.0	2.0	6.5	0.3	49	8.0
13	34	30	3.0	16	3.6	2.0	15	0.3	104	10
18	49	31	6	21	5	3	19	1.5	135	20
24	64	35	4	14	3	2	25	1.5	149	24
28	64	38	6.5	17	4	5	25	1.5	161	20
36	84	53	9	27	6	4	32	2	217	35
40	70	50	4	23	3	3	25	1	179	22
46	75	60	3	23	1	1	24	1	188	24

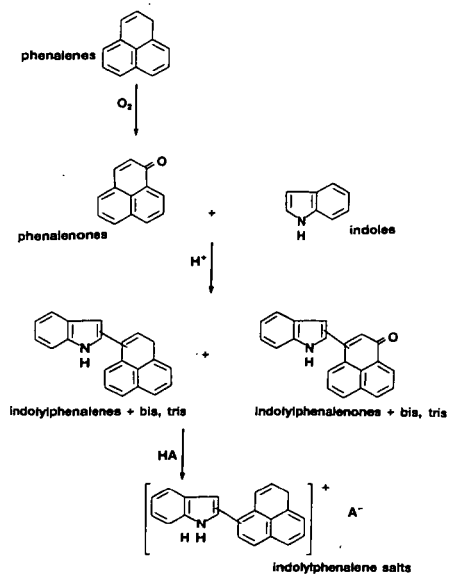


Figure 1. Reaction mechanism for sediment formation.

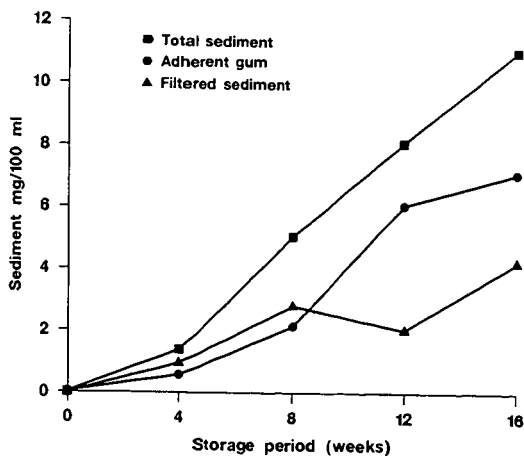


Figure 2. Changes in total sediment with time (bottle storage at 43°C).

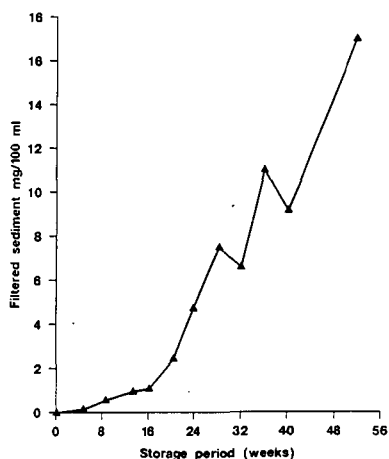


Figure 3. Changes in filtered sediment with time (drum storage).

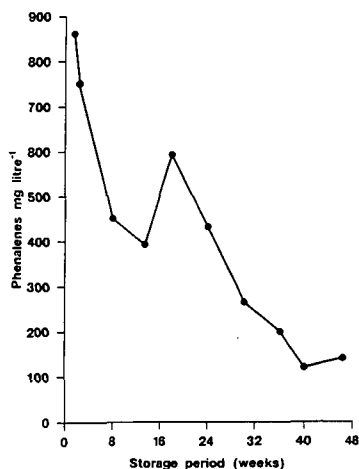


Figure 4. Changes in total phenalenes concentration with time (drum storage).

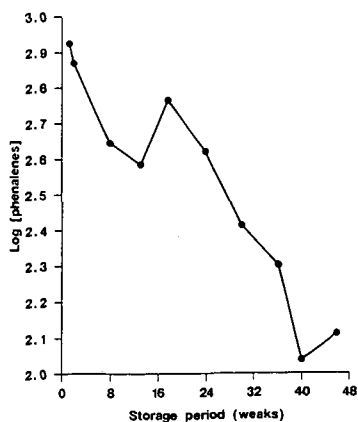


Figure 5. Changes in log [phenalenes] with time (drum storage).

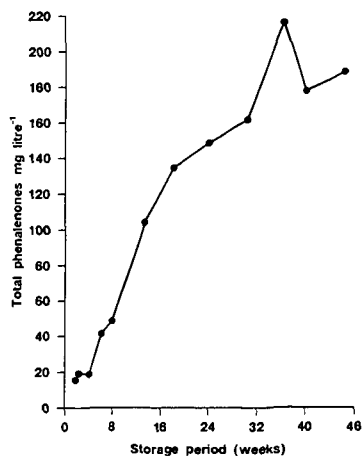


Figure 6. Changes in total phenalenones concentration with time (drum storage).



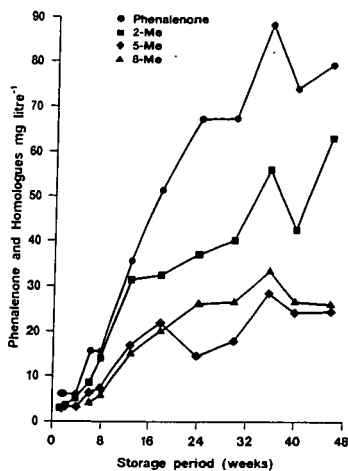


Figure 7. Changes in phenalenone and homologues concentrations with time (drum storage).

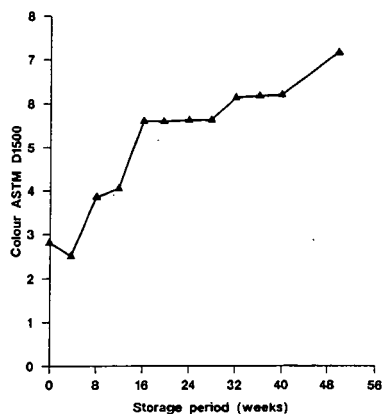


Figure 8. Changes in colour with time (drum storage).

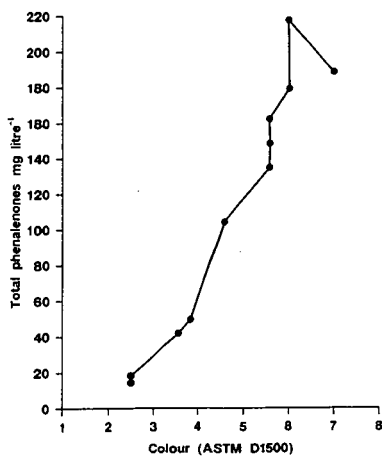


Figure 9. Changes in colour with total phenalenones concentration (drum storage).

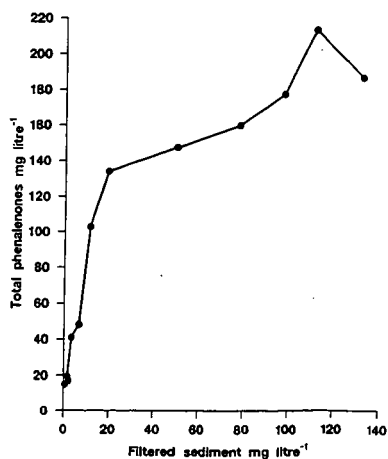


Figure 10. Changes in filtered sediment levels with total phenalenones concentration (drum storage).